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HYDROGEN PRODUCTION

Robert Jenkins Williams

Thesis  
.W62

Thesis  
W62

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January 20, 1914

## HYDROGEN PRODUCTION

A THESIS

Presented to the Faculty of the Graduate School of Cornell  
University for the degree of Master of Science in Engineering

By

Robert Jenkins Williams

June 21, 1946



Thesis  
W62

Proceedings of the National Academy of Sciences

BIOGRAPHICAL SKETCH OF THE AUTHOR

The author, Robert Jenkins Williams, was born on July 12, 1919 in Mannington, Kentucky. He attended Crofton High School, Crofton, Kentucky, and graduated in 1936. From 1937 until 1941 he was a student at the University of Louisville. In June, 1941 he was awarded the degree of Bachelor of Chemical Engineering from that institution. From June, 1941 until May, 1942 he was employed as a chemist by the E. I. duPont de Nemours & Co., Inc. in the Indiana Ordnance Works. In May, 1942 he was ordered to active duty in the United States Naval Reserve and has continued in that status during the past four years.



## Production of Hydrogen

### Introduction

Hydrogen is used in the hydrogenation of coal and of animal, vegetable and mineral oils; in the syntheses of ammonia, alcohol, and other organic chemicals; in the reduction of pure metals from ores; and in other commercial processes.

The process in which the hydrogen is to be used determines the purity of the hydrogen required. In operations involving catalyzed reactions, which include most of the hydrogenation reactions and syntheses, the hydrogen must be free of sulfur compounds because sulfur compounds act as catalyst poisons. In hydrogenation reactions involving the reduction of carbonyl and carboxyl groups, the presence of carbon monoxide and carbon dioxide in the hydrogen is relatively unimportant, but in the reduction of ethylenic linkages and in the synthesis of ammonia the hydrogen must be free of carbon oxides. The presence of hydrocarbon gases, such as methane, is not objectionable in most cases but reflects an



hydrogen is used in the hydrogenation of oils and in the synthesis of ammonia and other chemicals. It is also used in the production of methanol and in the synthesis of organic compounds. Hydrogen is a clean, renewable energy source and is used in the production of hydrogen fuel cells.

inefficiency of hydrocarbon conversion in steam-hydrocarbon processes for the manufacture of hydrogen. The presence of oxygen in more than a fraction of one per cent is very objectionable because of the explosive hazard of hydrogen-oxygen mixtures.

The need for hydrogen in quantity and of various degrees of purity has resulted in the development of several processes of producing hydrogen.

About twenty methods for quantity production of hydrogen have been proposed. Of these methods, only a few are economical enough for industrial use. The principal methods are:

- (1) The electrolysis of water
- (2) Liquefaction of coke-oven gas
- (3) Complete gasification of solid carbonaceous materials, such as coal or coke, producing carbon monoxide and hydrogen, with a subsequent reaction of the carbon monoxide with steam to produce carbon dioxide and additional hydrogen
- (4) Reaction of saturated hydrocarbon gases with steam to form hydrogen and carbon dioxide
- (5) Alternate oxidation and reduction of iron with steam and a reducing gas, such as water gas, to produce hydrogen from the steam.

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The electrolysis of water is carried out by the passage of an electric current through water containing either an alkali or an acid, with the liberation of hydrogen gas at the cathode and oxygen at the anode. This process is economical only where water power is cheap.

In the coking of coals, for each ton of coal coked about 11,000 cubic feet of gas of the following average composition are produced:

Component	Per Cent by Volume
Hydrogen	50
Methane	32
Carbon Monoxide	6.5
Carbon Dioxide	2.0
Nitrogen	5.0
Illuminants	4.0
Oxygen	0.5

The coke-oven gas is subjected to purification processes to remove impurities, such as  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCN}$ ,  $\text{HCl}$  and light oils, and then is fractionally liquefied to obtain hydrogen and fractions of carbon monoxide and hydrocarbons. The carbon monoxide and hydrocarbons are subjected to reaction with steam to produce additional hydrogen. Hydrogen is obtained in this manner as a by-product.

The steam-iron process of producing hydrogen is carried



The electrolysis is better in nature and to the purpose

of an electric current through which electricity is  
 applied or to supply with the electricity of hydrogen gas in the  
 liquid and gases of the water. This process is essential  
 help with water, even in large.

In the study of water, for each day of each water  
 10,000 cubic feet of gas of the following electric composition  
 are produced:

Composition	Gas (by volume)
Hydrogen	20
Oxygen	10
Carbon dioxide	0.5
Carbon monoxide	1.0
Nitrogen	1.0
Ammonia	1.0
Water	0.1

The composition for is subjected to purification processes  
 of water treatment, such as 100, 100, 100, and 100, and  
 the gas is (hydrogen) treated in which hydrogen and water  
 from of water treatment and hydrogen. The water now  
 and the hydrogen is subjected to water and steam  
 to produce additional hydrogen. Hydrogen is obtained in  
 this manner as a by-product.

The chemical process of producing hydrogen is varied

out in two stages. Steam is passed over iron at temperatures above 1200° F., oxidizing the iron to an iron oxide and liberating hydrogen. The iron oxide is reduced to iron by water gas, and is then steamed again. This is one of the earliest methods of producing hydrogen and is still in use for making small quantities of hydrogen (less than 1000 cubic feet per hour).

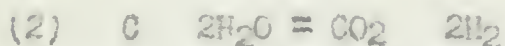
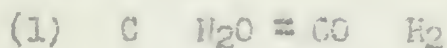
It is estimated that the quantity of hydrogen manufactured per month in the United States is six billion and four billion cubic feet by the water-gas and hydrocarbon-steam processes, respectively.<sup>2</sup>

The production of hydrogen from water gas and from saturated hydrocarbon gases will be discussed in this thesis.



## Water-Gas Manufacture for Hydrogen Production

Carbon may react with steam according to the following equations:



The reactions are endothermic and proceed only at elevated temperatures. The equilibriums of the two reactions are such that at temperatures above about 1500° F. the formation of carbon monoxide is favored, while the formation of carbon dioxide is favored by temperatures below 1500° F. This is apparent from the equilibrium for the reaction:



The equilibrium constant for this reaction is defined as:

$$K_p = \frac{(\text{CO}_2)(\text{H}_2)}{(\text{CO})(\text{H}_2\text{O})}.$$

At 1500° F.,  $K_p$  is 0.973; at 800° F.,  $K_p$  has a value of 11.93.

The velocity of Reaction (2) is so low at temperatures favoring the formation of carbon dioxide that it is not practicable, and Reaction (1) must be used.

The generator for making water gas consists of a steel shell, lined with firebrick, with gas outlet and steam inlet connections at top and bottom, and an air inlet at the bottom. Coke is fed automatically to maintain a fuel bed of the desired depth; ash is removed automatically. The coke is



the following conditions for the system:

1. The system is linear and time-invariant.

2. The system is causal.

3. The system is stable.

4. The system is invertible.

5. The system is minimum phase.

6. The system is all-pass.

7. The system is band-pass.

8. The system is low-pass.

9. The system is high-pass.

10. The system is band-stop.

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24. The system is low-pass.

25. The system is high-pass.

ignited and air is blown through the generator until the coke is at a temperature of about  $1800 - 2000^{\circ}$  F. The gases from this operation are led off as waste gas. After this temperature is reached, the air supply is cut off and steam is introduced into the generator at such a rate that the steam is nearly all decomposed in reacting with the coke to form water gas, which is collected by suitable means. This endothermic reaction reduces the temperature of the fuel bed in about five or six minutes. When the temperature has dropped to about  $1750^{\circ}$  F., steaming is stopped and air is blown through for about two minutes to raise the temperature to  $1800 - 2000^{\circ}$  F. again by combustion of some of the coke. Temperatures above  $2000^{\circ}$  F. result in excessive losses in carbon monoxide, while temperatures below  $1750^{\circ}$  F. result in excess carbon dioxide in the water gas.

One ton of coke produces about 60,000 cubic feet of water gas of about the following composition:

Component	Per Cent by Volume
Hydrogen	50 - 53
Carbon monoxide	39 - 43
Carbon dioxide	3 - 6
Nitrogen	0.6 - 4.6
Methane	0.2 - 0.3
Oxygen	0.1 - 0.2
Sulfur compounds	Traces.

1. The first step in the process of the investigation is the identification of the problem. This is done by the investigator who is responsible for the investigation. The investigator should identify the problem and the scope of the investigation. The investigator should also identify the objectives of the investigation and the methods to be used. The investigator should also identify the resources available for the investigation.

2. The second step in the process of the investigation is the collection of data. This is done by the investigator who is responsible for the investigation. The investigator should collect data from the sources identified in the first step. The investigator should also collect data from the sources identified in the first step. The investigator should also collect data from the sources identified in the first step.

3. The third step in the process of the investigation is the analysis of the data. This is done by the investigator who is responsible for the investigation. The investigator should analyze the data collected in the second step. The investigator should also analyze the data collected in the second step. The investigator should also analyze the data collected in the second step.

4. The fourth step in the process of the investigation is the interpretation of the results. This is done by the investigator who is responsible for the investigation. The investigator should interpret the results of the analysis in the third step. The investigator should also interpret the results of the analysis in the third step. The investigator should also interpret the results of the analysis in the third step.

5. The fifth step in the process of the investigation is the reporting of the results. This is done by the investigator who is responsible for the investigation. The investigator should report the results of the investigation to the appropriate authorities. The investigator should also report the results of the investigation to the appropriate authorities. The investigator should also report the results of the investigation to the appropriate authorities.

Figure 1

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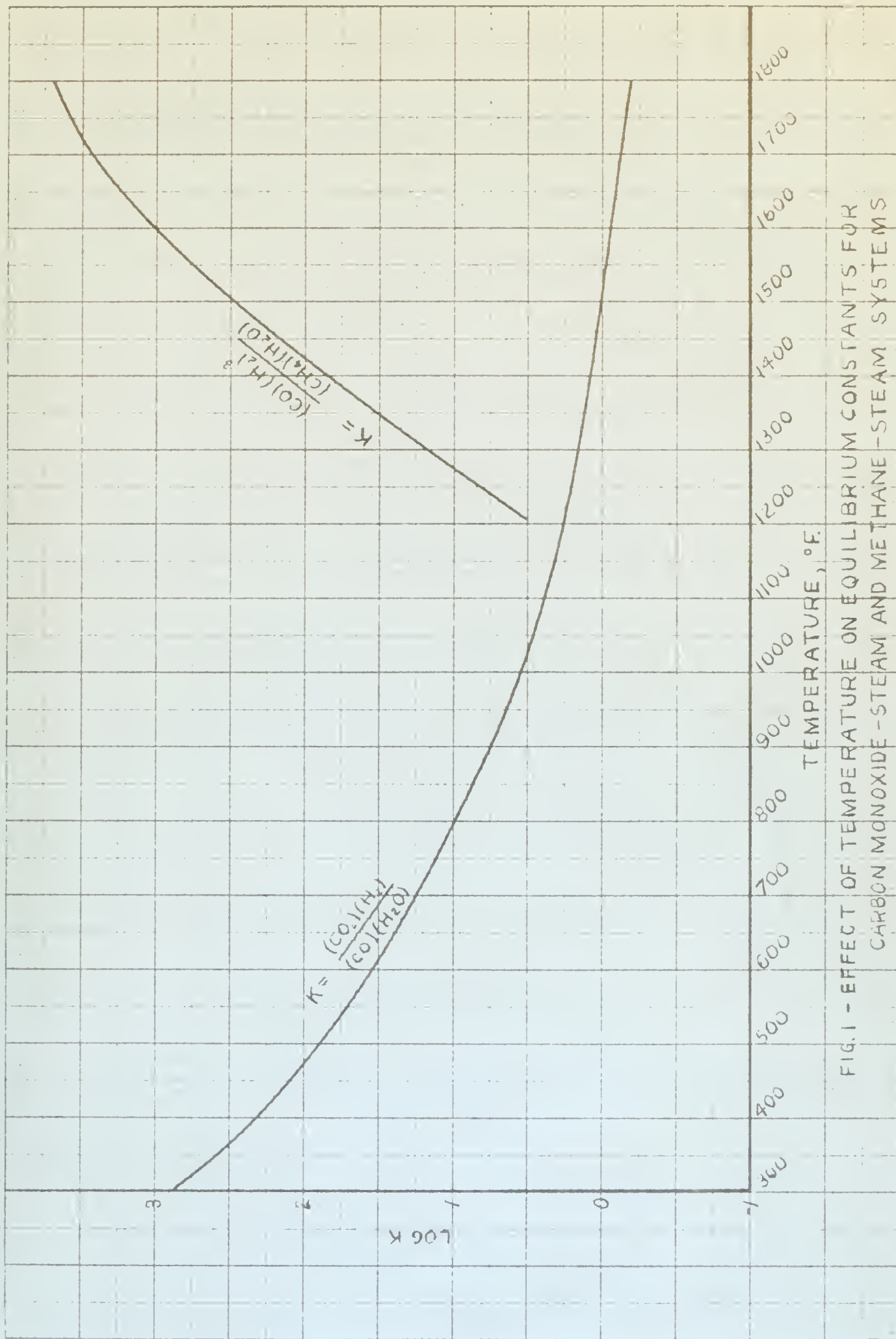


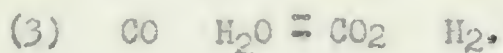
FIG. 1 - EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANTS FOR CARBON MONOXIDE-STEAM AND METHANE-STEAM SYSTEMS





## Hydrogen from the Water Gas - Steam Reaction

Carbon monoxide and steam react under suitable conditions of temperature and concentration as follows:



The reaction is endothermic at 68° F., requiring 5630 B.t.u. per pound mol, so that it must be carried out at elevated temperatures. At 700° F. the reaction is exothermic, liberating 16,500 B.t.u. per pound mol.<sup>3</sup> Figure 1 shows the effect of temperature on the equilibrium constant

$$K_p = \frac{(\text{CO}_2)(\text{H}_2)}{(\text{CO})(\text{H}_2\text{O})}.$$

Table I shows the effect of temperature and initial concentration of steam to carbon monoxide on the amount of carbon monoxide reacted at equilibrium as calculated from values of the equilibrium constant.

# Effect of Temperature on the Equilibrium Constant

The following data were obtained from the study of the reaction:

of hydrogen and iodine at various temperatures.

$$(2) \quad H_2 + I_2 \rightleftharpoons 2HI$$

The reaction is exothermic,  $\Delta H^\circ = -10.4$  kcal/mole  $H_2$ .

For each temperature, the initial concentrations of the reactants were 0.1 mole/l.

and the equilibrium constant was determined from the following data:

at 400°C,  $K_c = 50.0$ ; at 450°C,  $K_c = 26.0$ ; at 500°C,  $K_c = 16.0$ .

of hydrogen and iodine at various temperatures.

$$\ln K = \frac{\Delta H^\circ}{RT} + \ln K^\circ$$

Table 1 shows the effect of temperature on the equilibrium constant.

From the data in Table 1, the equilibrium constant was calculated for each temperature.

The equilibrium constant is independent of the initial concentrations of the reactants.

of the equilibrium constant.

Table I

Temperature °F.	Percentage of Carbon Monoxide Reacted with Starting Molar Ratios of Steam to Carbon Monoxide of:				
	1:1	2:1	3:1	5:1	9:1
932	69.1	87.3	91.7	95.4	97.6
842	73.3	90.0	94.4	97.0	98.4
800	75.0	91.5	95.2	97.5	98.7
752	77.5	93.0	96.4	98.0	99.0
662	82.0	95.7	97.9	99.2	99.9
620	84.0	96.7	98.2		
440	91.8	99.2	99.6		
260	97.5	99.9	99.96		

It can be seen that low temperatures (below 260° F.) favor the maximum conversion of carbon monoxide with the least amount of steam. At low temperatures, however, the rate of reaction of carbon monoxide with steam is so low as to be impracticable. At temperatures above 750° F. the reaction can be catalyzed to a practicable rate, but the conversion is less complete.

Various catalysts have been proposed for use in carrying out the water-gas reaction to produce hydrogen. (Quoted from the patent literature:



Table 1

Temperature of water in the bath, °C					Time, min
10	20	30	40	50	
10.0	10.0	10.0	10.0	10.0	10
10.0	10.0	10.0	10.0	10.0	20
10.0	10.0	10.0	10.0	10.0	30
10.0	10.0	10.0	10.0	10.0	40
10.0	10.0	10.0	10.0	10.0	50
10.0	10.0	10.0	10.0	10.0	60
10.0	10.0	10.0	10.0	10.0	70
10.0	10.0	10.0	10.0	10.0	80
10.0	10.0	10.0	10.0	10.0	90
10.0	10.0	10.0	10.0	10.0	100

It was found that the temperature of the water in the bath during the experiment is constant, and the rate of reaction is independent of the temperature of the water in the bath. This is due to the fact that the reaction is a zero-order reaction, and the rate of reaction is independent of the concentration of the reactants. The rate of reaction is determined by the rate of diffusion of the reactants into the reaction vessel, and this is independent of the temperature of the water in the bath. The rate of reaction is also independent of the concentration of the reactants, as the reaction is a zero-order reaction. The rate of reaction is determined by the rate of diffusion of the reactants into the reaction vessel, and this is independent of the temperature of the water in the bath. The rate of reaction is also independent of the concentration of the reactants, as the reaction is a zero-order reaction.

"Magnesium oxide is a catalyst for the carbon monoxide-steam conversion and that in this as well as other reactions involving carbon monoxide or hydrogen in which it functions catalytically, it is insensitive to the poisoning influence of sulfur.

The use of magnesium oxide as a catalyst in reactions involving carbon monoxide is especially advantageous in view of the fact that it causes little or no deposition of carbon under conditions where catalysts such as iron, nickel and cobalt become rapidly coated with carbon produced by decomposition of carbon monoxide."<sup>5</sup>

"The activity of an iron group metal oxide as a catalyst for the production of hydrogen from carbon monoxide and steam may be greatly improved by incorporating with an iron group metal oxide a metallic oxide, for example copper oxide or antimony oxide, reducible to the metal under the conditions of the hydrogen-making operation, and fusing the mixture. The material thus prepared, after suitable reduction treatment, shows an improved activity as a catalyst for the conversion of carbon monoxide and steam and under normal conditions remains active for a long time. Its behavior as a catalyst is superior not only to that of fused iron group metal oxide alone but also to that of a mixture of iron group metal and copper or antimony oxide prepared without fusion."<sup>6</sup>





"A mixture of charcoal (or substances containing carbon) and magnesium carbonate, which is maintained at a temperature above the decomposition temperature of magnesium carbonate, but not substantially exceeding  $500^{\circ}\text{C.}$ "?

"For the catalytical conversion of carbon monoxide with steam there have been proposed catalysts consisting of a mixture of magnesium oxide, carbon, and alkali carbonate, preferably potassium carbonate. With the aid of these very active catalysts the conversion of the carbon monoxide proceeds even at temperatures below  $500^{\circ}\text{C.}$  with useful velocities up to the point at which, practically speaking, complete establishment of the equilibrium is attained. This results in the advantage that in large scale working a low residual carbon monoxide content, according to the temperature, can be obtained without uneconomically high steam consumption. When working with these catalysts it is further also possible to effect the conversion, without the disadvantages of undesirable secondary reactions such as in particular deposition of carbon and formation of methane, under increased pressure, at the temperature most favorable for the conversion of carbon monoxide to carbon dioxide and hydrogen, and thus to effect a saving in reaction space and steam consumption. When other catalysts, and more particularly the known activated iron oxide catalysts, are used these secondary reactions set in



[illegible]

closely below  $500^{\circ}$  C. and rapidly reach an intolerable scale as the temperature falls,"<sup>8</sup>

"It has been found that the efficacy at the favorable working temperature below  $500^{\circ}$  C. of the known three-component catalysts magnesium oxide-alkali carbonate-carbon is enhanced to a very surprising extent by the accessory effect of iron oxide in the original state of native iron ores, that is to say without being brought into the state of finely divided artificial iron oxide, and that the above-mentioned native iron ores are capable of producing this effect when used in such small amounts that no deposition of carbon or methane formation occurs even when working under excess pressure and at the lowest applicable temperatures. Moreover, these four-component catalysts also retain undiminished the poison-resisting properties of the known three-component catalysts, more particularly in respect of the commonest catalyst poison, namely sulphur, in inorganic or organic combination.

The catalyst may for example have the following composition:

	Per Cent
MgO (in the form of calcined or caustic burnt magnesia)	13.5
Fe <sub>2</sub> O <sub>3</sub> (in the form of iron ore)	1.5
Potassium carbonate	15.0
Carbon	70.0. <sup>02</sup>



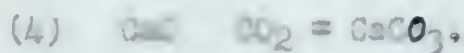


At the temperatures required for suitable catalyzed reaction velocities the carbon monoxide is incompletely converted at the equilibrium composition when a stoichiometric amount of steam is used. To obtain a higher conversion of carbon monoxide and a purer hydrogen one or more of the following methods may be used:

- (1) Using steam in excess of the stoichiometric amount<sup>9</sup>
- (2) Removing carbon dioxide as rapidly as it is formed<sup>10,11</sup>
- (3) Reacting in steps with carbon dioxide removal at the end of each step.<sup>2,3</sup>

The effect of using excess steam is shown in Table I. If hydrogen of high purity is desired this process is not economical because of the very large quantities of steam required.

The carbon monoxide can be completely converted by removing carbon dioxide as the reaction proceeds. Calcium oxide is generally used for removing the carbon dioxide. Steam and carbon monoxide are passed over lime containing a catalyst of the type described above at a temperature below the dissociation temperature (1517° F.) of calcium carbonate. The carbon dioxide formed by the carbon monoxide conversion reacts with the lime to form calcium carbonate as follows:



For complete conversion, all of the carbon dioxide



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formed must be reacted with an equivalent molar quantity of lime, so that in the conversion process there must be some means of bringing unreacted lime in contact with the water gas and of discharging the calcium carbonate, which is heated to form calcium oxide again.

The effect of carrying out the conversion in stages with removal of carbon dioxide at the end of each stage is shown by the calculated values below, using one mol of steam in each stage and starting with one mol of carbon monoxide in the first stage.

Stage	Temperature °F.	Mol Carbon Monoxide Converted
1.	800	.75
2.	800	.221
3.	800	.026
		<hr/> .997

It is seen that the steam consumption for a given degree of conversion of carbon monoxide is much less in a multi-stage process than in a single stage process.

It is found that the amount of water which is absorbed by the soil is not proportional to the amount of water which is applied. The amount of water which is absorbed by the soil is proportional to the square root of the amount of water which is applied. This is the law of diffusion.

The effect of the amount of water which is applied to the soil is to increase the amount of water which is absorbed by the soil. The amount of water which is absorbed by the soil is proportional to the square root of the amount of water which is applied. This is the law of diffusion.

Amount of water applied	Amount of water absorbed	Ratio
100	10	1
400	20	2
900	30	3
1600	40	4

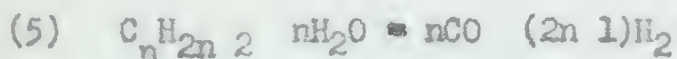
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## Production of Hydrogen from Hydrocarbons and Steam

The reactions between saturated hydrocarbon gases, such as methane, ethane, or propane, and steam have been found an economical and convenient means of producing hydrogen. The saturated hydrocarbons are the principal constituents of natural gas, coke-oven gas and waste gas from petroleum cracking processes. Where cheap natural gas is available, processes utilizing the steam-hydrocarbon reactions are the most economical methods of producing pure hydrogen in large quantities.<sup>12</sup>

The reactions which occur are:



Reaction (6) may be considered as Reaction (5) followed by the water-gas reaction



These reactions are endothermic and must be carried out at elevated temperatures. In Figure 1, it can be seen that at temperatures above 1500° F. the equilibrium constant

$$K = \frac{(CO)(H_2)^3}{(CH_4)(H_2O)}$$

is large, so that at equilibrium the methane must be nearly completely converted.



Proportion of Hydrogen from Hydrocarbons and Steam

The reaction between molecular hydrogen and steam is reversible, and the equilibrium constant is a function of temperature. The equilibrium constant for the reaction is given by the following equation:

$$K_p = \frac{p_{H_2} p_{H_2O}}{p_{H_2O}^2}$$

where  $p_{H_2}$  is the partial pressure of hydrogen,  $p_{H_2O}$  is the partial pressure of steam, and  $K_p$  is the equilibrium constant. The equilibrium constant is a function of temperature and is given by the following equation:

$$\log K_p = \frac{10,000}{T} - 1.75$$

where  $T$  is the temperature in degrees Kelvin. The equilibrium constant is a function of temperature and is given by the following equation:

$$\log K_p = \frac{10,000}{T} - 1.75$$

The reaction is reversible and the equilibrium constant is a function of temperature.

$$(1) \quad \log K_p = \frac{10,000}{T} - 1.75$$

$$(2) \quad \log K_p = \frac{10,000}{T} - 1.75$$

Equation (1) is the equilibrium constant for the reaction of hydrogen and steam.

Equation (2) is the equilibrium constant for the reaction of hydrogen and steam.

$$\log K_p = \frac{10,000}{T} - 1.75$$

These two equations are identical and can be used to calculate the equilibrium constant for the reaction of hydrogen and steam.

It should be noted that in Figure 1, it was assumed that the reaction is reversible and the equilibrium constant is a function of temperature.

Equation (1) is the equilibrium constant for the reaction of hydrogen and steam.

$$K_p = \frac{p_{H_2} p_{H_2O}}{p_{H_2O}^2}$$

Equation (2) is the equilibrium constant for the reaction of hydrogen and steam.

Equation (3) is the equilibrium constant for the reaction of hydrogen and steam.

Catalysts must be used to give a practicable rate of reaction. German Patent No. 296,866 of 1912 proposed a catalyst of nickel or nickel oxide on a refractory support. The following material on catalysts for the hydrocarbon-steam reactions is quoted from the patent literature:

"Nickel alone even with the exclusion of chlorine and other catalyst poisons is not very active for the production of hydrogen by a reaction between steam and hydrocarbons at temperatures below  $700^{\circ}\text{C}.$ .... by the addition of ... promoters ( ... cerium oxide, ... chromium oxide, ... aluminum oxide ...) the catalytic behavior of nickel in this reaction can be improved to the extent that the conversion of hydrocarbons into hydrogen becomes practicable at temperatures materially below  $700^{\circ}\text{C}.$ .... The operation can be conducted ... at higher temperatures. ... Certain substances greatly decrease or even completely inhibit the activity of nickel catalysts for this purpose. Among such substances are the halogens, such as chlorine, and compounds of sulfur."<sup>13</sup>

" ... a compound of nickel and chromium oxide such as nickel chromate is a more active catalyst than a mixture of nickel and chromium oxide."<sup>14</sup>

"The catalyst used is ordinarily a mixture of nickel or cobalt oxides with alumina or thoria ... "<sup>15</sup>

"Suitable catalysts for the production of hydrogen should





possess high activity and great physical strength, and should shrink very little at the operating temperature used. Oxides or metals of the iron group, admixed with aluminum oxide, form desirable catalyst. Calcium and magnesium oxides and silica may be added to secure catalysts of greater strength at high temperatures. Phosphoric acid with alumina and nickel oxide produces a very active catalyst which shrinks very little at high temperatures. A specially suitable catalyst is prepared from nickel oxides, magnesia and kaolin."<sup>16</sup>

The equilibrium compositions in the methane-steam reaction, starting with one mol of methane and two mols of steam, have been calculated for various temperatures and are given in Table II<sup>3</sup> on a dry basis.

Table II

## Equilibrium Compositions in The Methane-Steam Reaction

Component	Percentage Composition					
	985° F.	1340° F.	1500° F.	1600° F.	1700° F.	1800° F.
H <sub>2</sub>	61	75.8	76.1	76.1	75.9	75.9
CH <sub>4</sub>	23	1.0	0.1	0.04	0.01	0.01
CO	4	17.2	19.1	19.7	20.3	20.7
CO <sub>2</sub>	12	6.0	4.7	4.2	3.8	3.4





From a study of equilibrium data for the hydrocarbon-steam reactions, it can be seen that the maximum yield of hydrogen can be obtained by one or more of the following methods:

- (1) Reacting at temperatures favoring the formation of carbon dioxide and using steam in excess of the stoichiometric amount
- (2) Reacting at temperatures favoring the formation of carbon dioxide and removing the carbon dioxide as rapidly as it is formed
- (3) Reacting at temperatures favoring the formation of carbon monoxide and then converting the carbon monoxide as previously described.

The processes using excess steam are not as economical and do not give as high conversion of hydrocarbons as other processes. The reaction is generally carried out using a 10 to 1 to 15 to 1 volume ratio of steam to hydrocarbon, temperatures below about 1300° F. and pressures of from 1 to 50 atmospheres. Although low pressures favor the conversion of hydrocarbons, high pressures may be used to reduce heat losses.<sup>17,18,19,20</sup>

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Processes based on the removal of carbon dioxide as rapidly as formed are described in the patent literature. The product from these processes contains at least two per cent methane.<sup>11,12</sup> The author has found no references in the technical literature on the commercial application of these methods.

The processes involving the reaction of hydrocarbons with steam at temperatures above 1500° F. to form carbon monoxide, with the subsequent conversion of the carbon monoxide at temperatures below 900° F., are capable of producing hydrogen of high purity more economically than can other hydrocarbon conversion processes. A plant with a capacity of 13,000,000 cubic feet per day has been described.<sup>22,23</sup>

A mixture of equal parts, by volume, of gas and steam, at atmospheric pressure, passes downward through vertical alloy-steel tubes packed with a catalyst of the nickel type. The tubes, about 25 feet long and 6 inches in diameter, are placed in two rows in a refractory-lined furnace and are supported at their tops. The furnace is heated by gas burning at the top of the furnace and between the rows of tubes.<sup>16</sup> The natural gas and steam, flowing downward through the tubes at space velocities up to 300 volumes of hydrocarbon gas per hour per volume of catalyst, react nearly completely and leave the bottom of the tubes at about 1750° F. with about the





following composition:

Component	Per Cent (Dry Basis)
Hydrogen	73.
Carbon monoxide	15.
Carbon dioxide	10.
Methane	1.
Nitrogen	1.

After this reaction, more steam is added and the carbon monoxide is converted to carbon dioxide at about 850° F. by a catalytic water-gas reaction. The resulting gas mixture, containing about 78 per cent hydrogen, 20 per cent carbon dioxide, and 2 per cent unconverted methane and carbon monoxide, is then cooled with water in coke-packed towers, compressed to 250 pounds per square inch and scrubbed in a bubble tower with a monoethanolamine solution to remove carbon dioxide. The product has about the following composition:

Component	Per Cent
Hydrogen	75 - 97
Carbon monoxide	1.5 - 2.0
Methane	1 - 1.5
Nitrogen	0 - 1.5
Carbon dioxide	Trace.

Category	Percentage
Unemployed	7.5
Retired	12.5
Disabled	15.0
Homebound	1.0
Other	1.0

These data indicate that about 15% of the population is unemployed, 12.5% is retired, 15% is disabled, 1% is homebound, and 1% is in other categories. The total percentage of the population in these categories is 47%. The remaining 53% of the population is employed. The data also indicate that the percentage of the population in each category is relatively small, with the largest category being the unemployed at 7.5%.

Category	Percentage
Unemployed	7.5
Retired	12.5
Disabled	15.0
Homebound	1.0
Other	1.0

A process for the production of pure hydrogen, utilizing the hydrocarbon-steam reaction with the subsequent conversion of carbon monoxide, has been developed.<sup>3</sup> This process uses commercial propane as process material and as fuel.

Propane vapors, heated to about 700° F., are passed over over bauxite or metallic oxide catalysts for the conversion of organic sulphur compounds to hydrogen sulphide. The vapor is then cooled and scrubbed with a caustic solution to remove the hydrogen sulphide.

The sulfur-free propane is mixed with steam and passed downward over the catalyst in the tubes of a Shapleigh<sup>21</sup> furnace. This furnace consists of catalyst-filled nickel-chromium-iron alloy tubes placed vertically and supported at their tops in a refractory-lined shell. Gas burners are placed in the furnace tangentially to the walls so that the combustion gases are given a spiralling upward motion around the tubes and along the furnace walls. With this furnace, space velocities of about 600 volumes of hydrocarbon per hour per volume of catalyst are attained with temperatures above about 1600° F. in the reaction gases.

These reaction gases, cooled to about 700° F. with steam, are passed over a catalyst, at space velocities of 100 or more volumes of carbon monoxide and hydrogen per hour per volume of catalyst, for conversion of the carbon monoxide to carbon



It is a pleasure to have you here, and we are sure you will find the trip well worth the effort.

the following table.

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dioxide. After this reaction the excess steam is condensed and the gases are cooled to about 100° F. and passed through a scrubber to remove carbon dioxide.

The carbon dioxide is absorbed by scrubbing with a solution of 15 to 20 per cent of monoethanolamine in water. After scrubbing, the gas contains about one per cent of carbon monoxide, which is removed in two more stages of carbon monoxide conversion and carbon dioxide removal.

The hydrogen produced by this process has about the following composition:

Component	Per Cent
Hydrogen	99.958
Methane	0.015
Carbon dioxide	0.001
Carbon monoxide	0.001
Nitrogen	0.007
Oxygen	0.005
	<u>100.000.</u>



### Conclusions

The hydrocarbon-steam process provides the most economical and convenient means of producing hydrogen in the United States. It has been developed to such an extent that it is used almost exclusively in new installations.<sup>2</sup>

Among the advantages of the process are: continuous and automatic operation resulting in minimum labor costs; high purity of hydrogen obtainable; and simplicity of mechanical design.



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